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INTERNAL REPORT PM-I-62-5

# OBSERVATIONS ON THE CORROSION OF ZIRCALOY-2, CONTAINING PALLADIUM AND GOLD

by

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## SUMMARY OF RESULTS

Zircaloy-2 samples containing 0.062 wt % Pd and 0.106 wt % Au were corrosion tested in steam at 400°C (750°F) and 1500 psi for 1240 hr. No significant improvementsin corrosion resistance or hydrogen pick-up were observed.

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## INTRODUCTION

At the present time, zircaloy-2 is considered to be the most attractive material available for use as fuel sheathing and pressure tubing in water-cooled natural uranium nuclear reactors. However, to keep up with reactor design, considerable work is being done to develop zirconium alloys with greater strength than zircaloy-2 and with as good or better corrosion resistance.

Stern and Wissenberg[1] demonstrated that alloying titanium with small amounts of the noble metals produced a material with corrosion resistance to both oxidizing and reducing type media. Because zirconium is physically and chemically very similar to titanium, an investigation of the effect of small additions of palladium and gold on the corrosion resistance of zircaloy-2 was considered.

This report describes the effect of additions of 0.062 wt % Pd and 0.106 wt % Au on the corrosion resistance of zircaloy-2 in steam at 400°C (750°F) and 1500 psi.

## PROCEDURE

Materials used for the alloys are listed in Table 1. The zircaloy-2 was in the form of thick wall tubing which had been obtained for development work.

TABLE 1

Materials

| Metal | Purity | Source |
|---|---|---|
| Zircaloy-2 | - | Atomic Energy of Canada Limited |
| Palladium | 99% | Johnson-Matthey and Mallory Limited |
| Gold | pure | Handy and Harman of Canada Limited |

The alloys containing palladium and gold and listed in Table 2 were prepared by arc melting 75 g buttons of zircaloy-2 in an argon atmosphere at a pressure of 350 mm of mercury, using a tungsten electrode and a cold copper hearth. The palladium and gold were added to the zircaloy-2 buttons and remelted four times to ensure homogeneity.

TABLE 2

Alloy Composition

| Alloy | Nominal Composition, wt % | Chemical Analysis, wt % |
|---|---|---|
| Zr-2 | - | - |
| Zr-2 + Pd | 0.056 Pd | 0.062 |
| Zr-2 + Au | 0.110 Au | 0.106 |

The buttons were hot rolled at 500°C (930°F) to 0.137 in. sheet from which two specimens (1 in. x 7/8 in. x 1/8 in.) of each alloy were machined.

Corrosion tests were carried out in an autoclave in steam at 400°C (750°F) and 1500 psi for times up to 1240 hr. Periodically, the specimens were removed for weighing and the water was changed after each weighing.

Hydrogen determinations by the vacuum-fusion method were done on the hot rolled sheet and on the specimens after they had been corrosion tested for 1240 hr.

## RESULTS

The graph in Figure 1 (weight gain versus duration of exposure), shows the results of the corrosion tests, and the amount of hydrogen pick-up during corrosion is given in Table 3.

TABLE 3

Hydrogen Pick-Up During Corrosion in Steam at 400°C (750°F) and 1500 psi

| Alloy | Wt % $H_2$ | | Available $H_2$ Pick-Up, % | Time of Test (hr) |
|---|---|---|---|---|
| | Before Corrosion | After Corrosion | | |
| Zr-2 | 0.0021 | 0.0037 | 23 | 1240 |
| Zr-2-0.062 Pd | 0.0021 | 0.0053 | 35 | 1240 |
| Zr-2-0.106 Au | 0.0022 | 0.0043 | 27 | 1240 |

From the graph in Figure 1 it can be seen that the addition of palladium and gold caused a decrease in the corrosion resistance of zircaloy-2 in steam at 400°C (750°F) and 1500 psi. Table 3 shows the total hydrogen pick-up and the hydrogen pick-up as a percentage of the hydrogen available from the corrosion reaction; both increased with the addition of palladium or gold.

## DISCUSSION

Stern and Wissenberg[1], propose a theory to explain the role of the noble metals in increasing the corrosion resistance of titanium. It is suggested that the noble metal alloy additions form sites of low hydrogen overvoltages on the alloy surface, and create galvanic couples with potentials higher than the critical potential necessary for passivity of titanium in reducing type media.

In addition, titanium alloyed with noble metals becomes passive in environments with concentrations of oxidizing agents insufficient to passivate unalloyed titanium.

Union Carbide Metals Company has had patents granted[2,3] on the action of noble metals in preventing embrittlement of a series of metals, including titanium, under the action of hydrogen in aqueous media.

It appeared possible that noble metal additions might also have a significant effect in gaseous environments. Then because zirconium is a sister element to titanium, noble metal additions might have a beneficial effect on the corrosion behaviour and hydrogen pick-up of zircaloy-2 when tested in steam at 400°C (750°F) and 1500 psi. The results of this investigation did not support this suggestion.

The samples used in this investigation were forwarded to Chalk River for further testing at the request of Dr. F.H. Krenz.

## CONCLUSIONS

Alloying of 0.062 wt % Pd or 0.106 wt % Au to zircaloy-2 resulted in no significant improvement in corrosion resistance or hydrogen pick-up on exposure to steam at 400°C (750°F) and 1500 psi.

## ACKNOWLEDGEMENT

This work was performed under the direction of Mr. N.S. Spence, Head, Nuclear Metallurgy Section. The production of alloy melts and corrosion testing were done by W.H. Hutchings and W. Koops.

## REFERENCES

1. Milton Stern and Herman Wissenberg. The Influence of Noble Metal Alloy Additions on the Electrochemical and Corrosion Behaviour of Titanium. J. Electrochem. Soc. 106(9), 759 (1959).

2. French Patent 1,248,339. Platinum-Metals Review 6(1), 40 (1962).

3. French Patent 1,248,340. Platinum Metals Review 6(1), 40 (1962).

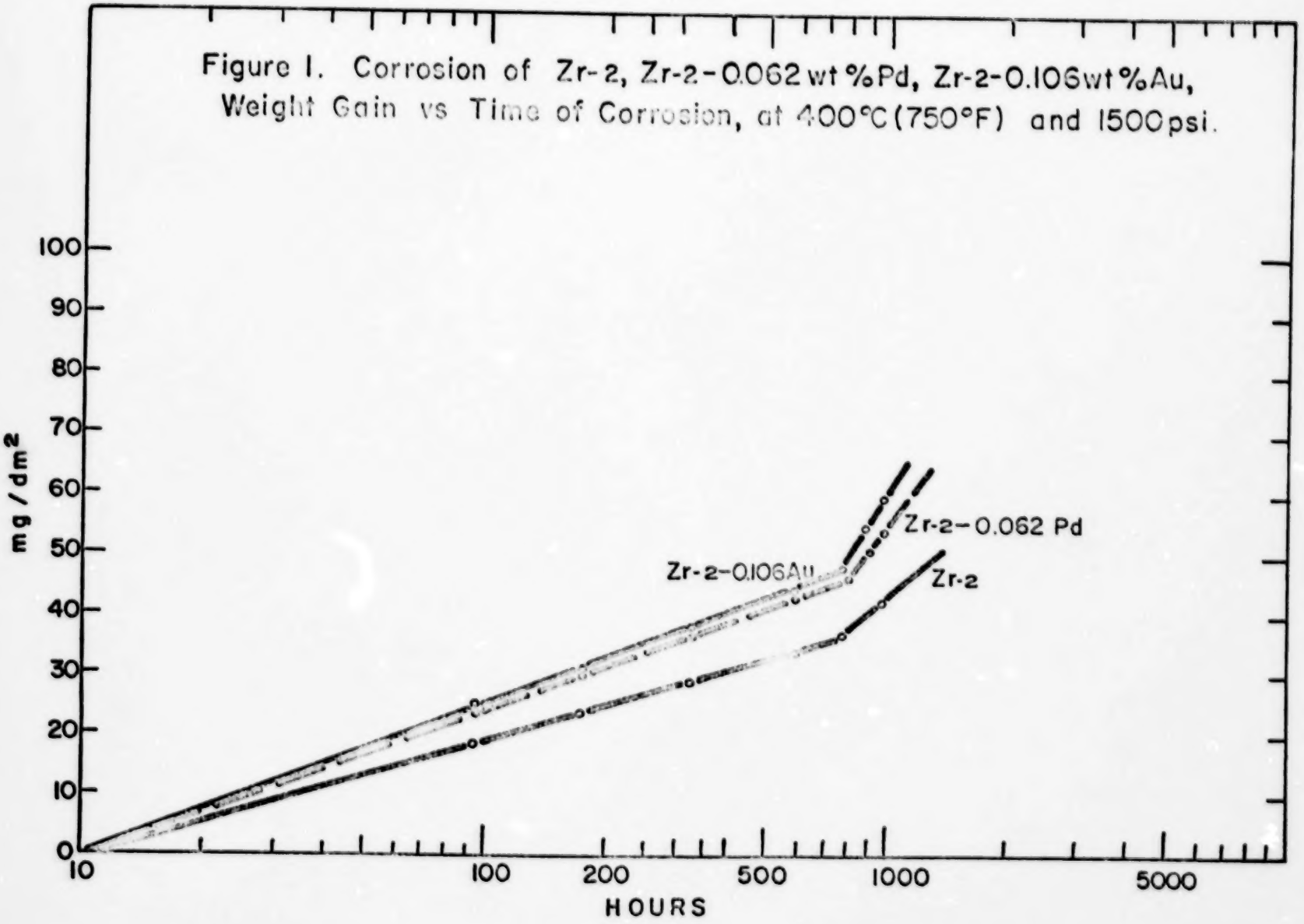
Figure I. Corrosion of Zr-2, Zr-2-0.062 wt % Pd, Zr-2-0.106 wt % Au, Weight Gain vs Time of Corrosion, at 400°C (750°F) and 1500 psi.
mg/dm²
100
90
80
70
60
50
40
30
20
10
0
10
100
200
500
1000
5000
HOURS
Zr-2-0.106Au
Zr-2-0.062 Pd
Zr-2